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(54) MEMBRANE CATALYST LAYER FOR FUEL CELLS

KATALYTISCHE MEMBRANSCHICHT FÜR BRENNSTOFFZELLEN

COUCHE CATALYSEUR MEMBRANE POUR PILES A COMBUSTIBLE

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(56) References cited:

US-A- 3 134 697 **US-A- 4 215 183**
US-A- 4 262 063 **US-A- 4 369 103**
US-A- 4 804 592 **US-A- 4 876 115**

- **SOLID STATE IONICS**, vol. 35, no. 1/2, July 1989, **AMSTERDAM NL** pages 3 - 9 **P. ALDEBERT ET AL 'PREPARATION AND CHARACTERIZATION OF SPE COMPOSITES FOR ELECTROLYZERS AND FUEL CELLS'**

- **JOURNAL OF THE ELECTROCHEMICAL SOCIETY** vol. 135, no. 9, September 1988, **MANCHESTER, NEW HAMPSHIRE US** pages 2209 - 2214 **E. A. TICIANELLI ET AL 'Methods to Advance Technology of Proton Exchange Membrane Fuel Cells'**
- **EXTENDED ABSTRACTS** vol. 89, no. 1, 7 May 1989, **PRINCETON, NEW JERSEY US** pages 36 - 37 **M.A. ENAYETULLAH ET AL 'Alternate Methods for Platinum Localization in Electrodes to Attain High Power Densities in Solid Polymer Electrolyte Fuel Cells'**
- **PROCEEDINGS OF THE 26TH INTERSOCIETY ENERGY CONVERSION ENGINEERING CONFERENCE** vol. 3, 4 August 1991, **BOSTON, MASSACHUSETTS** pages 636 - 641 **M. S. WILSON ET AL 'RECENT ACHIEVEMENTS IN POLYMER ELECTROLYTE FUEL CELL (PEFC) RESEARCH AT LOS ALAMOS NATIONAL LABORATORY'**
- **ALAMOS NATIONAL LABORATORY'**
- **Journal of Applied Chemistry**, Vol. 19, pp. 383-386 (1989), **SHULKA et al., 'A Nation-bound platinumized carbon electrode for oxygen reduction in solid polymer electrolyte cells', see page 385, subheading 2.3.**
- **Analytical Chemistry**, Vol. 58, pp. 2569-2570 (1986), **MOORE et al., 'Procedure for Preparing Solution-Cast Perfluorosulfonate Ionomer Films and Membranes'.**

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EP 0 600 888 B1

Description

BACKGROUND OF INVENTION

This invention relates to fuel cells and, more particularly, to catalyst loadings for solid polymer electrolyte fuel cells. This invention is the result of a contract with the Department of Energy (Contract No. W-7405-ENG-36).

Fuel cells are energy conversion devices presently being considered as one alternative to internal combustion engines. One type of fuel cell uses a solid polymer electrolyte (SPE) membrane, or proton exchange membrane, to provide ion exchange between the cathode and anode electrodes. Gaseous fuels may be used within the fuel cell, particularly hydrogen (H_2) and oxygen (O_2), where the electrodes are formed of porous conductive materials, e.g., woven graphite, to enable the fuel to disperse over the face of the SPE.

SPE fuel cells offer many advantages over liquid electrolyte fuel cells, including greater ultimate power densities, lower operating temperatures, and longer operating lifetimes. SPE materials are also generally resistant to corrosion and easy to incorporate into fuel cell structures. However, the anode and cathode half-cell reactions, H_2 and O_2 reactions, respectively, require catalysts to proceed at useful rates. As described in U.S. Patent 4,876,115, issued October 24, 1989, and incorporated herein by reference, catalyst materials were first incorporated by hot pressing the materials directly into the surface of the SPE membrane. Useful current densities in conventional SPE fuel cells were achieved only with high catalyst loadings, e.g., 4 mg Pt/cm². Since the catalyst materials are from the platinum group, with platinum being the preferred catalyst, these SPE fuel cells (herein referred to as GE/HS-UTC-type fuel cells) have not been cost competitive with other energy sources.

The '115 patent is directed to reducing the required platinum loading where the platinum is provided as platinum loaded carbon particles on a carbon cloth or carbon paper electrode substrate bound together by a hydrophobic component, such as polytetrafluorethylene (PTFE). The catalyzed sides of the carbon electrodes are impregnated to a depth of about 10 μ m with a solubilized form of the SPE to increase the access of the electrolyte to the platinum within the Pt-C/teflon catalyst layer. Indeed, catalyst loadings down to 0.35 mg/cm² of SPE area are reported to provide performance equivalent to conventional fuel cell catalyst loadings of 4 mg/cm².

The platinum catalyst is, however, not efficiently utilized in the prior art structures. It is difficult to match the impregnation depth of the SPE with the erratic thickness of a typical catalyst layer. This results in areas that are not fully impregnated and other areas where the SPE material extends deeper into the electrode than the catalyst layer and impedes gas diffusion through the electrode. Further, the hydrophobic binder blocks proton and

oxygen access to catalyst sites in cathode electrodes.

Another problem with prior art fuel cells is differential swelling between the SPE and the catalyst layer arising from the differing hydration characteristics between the hydrophilic SPE membrane and the carbon-based electrode structure. Delamination can occur between the SPE membrane and the electrode with a resulting discontinuity in the ion path and decreased cell longevity.

These problems are addressed by the present invention and a catalyst layer is provided adjacent a fuel cell SPE that is hydrophilic, contains substantially no cavities, is uniformly thin, and contains a uniform ratio of binder ionomer to supported catalyst.

Accordingly, it is an object of the present invention to provide a SPE fuel cell with relatively low supported catalyst loadings with no reduction in performance.

It is another object of the present invention to provide uniform continuity of electronic and ionic paths about all of the catalyst sites.

Still another object of the present invention is to provide a uniform dispersion of the supported catalyst layer in the binder layer.

One other object of the present invention is to improve the bonding between the SPE membrane and the catalyst layer.

Yet another object of the present invention is to provide a thin catalyst layer for adequate oxygen transport to all the catalyst sites through the ionomer binder material.

Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION

To achieve the foregoing and other objects, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the apparatus of this invention may comprise a gas reaction fuel cell having a solid polymer electrolyte for separating anodic and cathodic electrodes, wherein the improvement comprises a film of a proton conducting material with a thickness less than about 10 μ m and having a supported platinum catalyst uniformly dispersed therein with a platinum loading less than about 0.35 mg/cm², where said film is disposed between the solid polymer electrolyte and at least the cathodic electrode. A preferred film thickness is less than 5 μ m.

In another characterization of the present invention, a SPE fuel cell using hydrogen and oxygen is formed with a catalyst layer fabricated as a separate unit. A selected loading of supported Pt catalyst is uniformly dis-

persed in an ionomer that is effective for oxygen permeation and for ion transport, where the resulting mixture is formed as a thin film. The thin film is then transferred to the surface of a SPE membrane. The fuel cell is completed by urging a porous electrode structure against the catalyst film for oxygen transport through the ionomer to the catalyst sites.

In yet another characterization of the present invention, a SPE fuel cell using hydrogen and oxygen is formed using a Na⁺ form of a perfluorosulfonate ionomer to fabricate a catalyst layer. A supported Pt catalyst and a solvent are uniformly blended with the Na⁺ form of the ionomer to form an ink. The ink is applied to form a layer over a surface of the SPE membrane, also in the Na⁺ form. The layer is then dried at a temperature of at least 150°C for a time effective to dry the ink. The resulting film and membrane are converted back to the protonated form of the ionomer to form a pliant, elastic, and coherent catalytic layer on the SPE membrane.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of the specification, illustrate an embodiment of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

FIGURE 1 is a cross section of a fuel cell having a structure in accordance with one embodiment of the present invention.

FIGURE 1A is a pictorial illustration showing a magnified view of the catalyst layer according to the present invention.

FIGURE 2 graphically depicts the performance of a thin catalyst film with 0.20 mg/cm² and a thicker catalyst film with 0.35 mg/cm² of platinum on a first SPE.

FIGURE 3 graphically compares performance of thin catalyst films with 0.15 and 0.22 mgPt/cm² on a second SPE.

FIGURE 4 graphically compares the performance of a thin film cathode according to the present invention with 0.15 mgPt/cm² and a commercial gas-diffusion cathode with 0.35 mgPt/cm².

FIGURE 5 graphically depicts the performance of a fuel cell with a high-temperature formed, thin film catalyst layer with 0.17 gm Pt/cm²/electrode on Membrane "C".

FIGURE 6 graphically depicts the performance of a fuel cell with a high temperature formed, thin film catalyst layer with 0.13 mg Pt/cm²/electrode on a Dow membrane.

FIGURE 7 graphically compares the specific activity from a fuel cell according to the present invention and prior art fuel cells.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, a gas re-

action fuel cell includes a catalyst layer adjacent the cathode surface of a solid polymer electrolyte membrane to optimize utilization of the catalyst and to minimize the amount of the included catalyst. As shown in Figures 1 and 1A, catalyst layer 22 addresses three criteria necessary for a catalyst to efficiently contribute to the electrochemical processes in a fuel cell: proton access to the catalyst, gas access, and electronic continuity.

Fuel cell assembly 10 utilizes a gas fuel source 12, gas oxidizer source 14, solid polymer electrolyte (SPE) membrane 26 between porous anode backing structure 16 and porous cathode backing structure 18, and at least catalyst layer 22, according to the present invention, between the cathode surface of SPE 26 and cathode backing 18. It will be understood that catalyst layer 30 may be disposed between membrane 26 and anode backing structure 16. The foregoing discussion applies also to catalyst layer 30, although catalyst loadings for the anode may be only about one-half the catalyst loadings required for the cathode structure. Catalyst layer 22 is formed as a film of an proton conductive ionomer 28 and a supported platinum (Pt) catalyst 24 uniformly dispersed in ionomer 28 to assure that a uniform and controlled depth of the catalyst is maintained. The resulting film is a dense film of ionomer 28 and supported catalyst 24, i.e., there are no substantial voids in the film and there are no hydrophobic additives, such as PTFE, that block access of the diffusing gas and protons to the Pt catalyst sites. Gas access to the Pt catalyst sites is obtained through porous cathode backing structure 18 and by diffusion through ionomer 28. A suitable ionomer, such as a perfluorosulfonate ionomer, has sufficient oxygen permeability that a diffusion pathway length of 5-10 μm does not introduce any significant oxygen transport losses through the film for an oxygen gas.

Proton penetration and gas diffusion effects of electrolyte layers, as well as the relationship between volume fraction of ionomer 28 and potential drop within catalyst layer 22, indicate that an optimum catalyst layer 22 is very thin, i.e., less than 10 μm, and has a high volume density of supported catalyst 24 with the ionomer 28 in the interstices, i.e., the supporting carbon particles 25 are in contact with adjacent particles to form a low resistance electronic path through catalyst layer 22. A weight ratio of about 1:3 perfluorosulfonate ionomer (dry)/Pt-C is preferred for 20 wt% supported Pt. A dense film 22 is formed that is substantially free of cavities or water pockets that will lower the ionic and electronic conductivities. It will be appreciated that the thickness of film 22 is optimized when the thickness is equal to the active region for the half-cell reaction at any given current density and may be selected on the basis of the expected operating characteristics to match the catalyst thickness with a predetermined operating current density.

In one embodiment, film 22 is formed from an ink preparation including the supported catalyst, a solubi-

lized ionomer, and one or more volatile or decomposable suspension materials to provide a viscosity suitable for film formation. The ink is spread over a release blank in one or more layers to provide a preselected concentration of catalyst. A preferred protocol is as follows:

PROTOCOL I

1. Combine a solubilized perfluorosulfonate ionomer, such as Nafion (a registered trademark of E.I. duPont Nemours) in 5% solution (from Solution Technology, Inc.) and a supported catalyst (19.8 wt % platinum on carbon from Prototech Company, Newton Highlands, Massachusetts) in a weight ratio of 1:3 Nafion (dry)/Pt-C.
2. Add water and glycerol to weight ratios of about 1:5:20 for carbon/water/glycerol.
3. Agitate the mixture with ultrasound to uniformly disperse the supported catalyst in the ink and to form the mixture to a viscosity suitable for coating the release blank.
4. Clean a release blank of teflon film and coat the blank with a thin layer of mold release (e.g., a TFE spray). Paint the blank with a layer of ink and bake in an oven at 135°C until dry. Add layers until the desired catalyst loading is achieved.
5. Form an assembly of a polymer electrolyte membrane, counter electrode (anode electrode), and the coated blank. Place the assembly into a conventional hot press and lightly load the press until the press heats to a selected temperature (i.e., 125°C for Nafion and 145°C for "C" SPE material) and then press at 70-90 atm for 90 seconds.
6. Cool the assembly and then peel the release blank from the film, leaving the film adhered to the SPE membrane cathode surface.
7. An uncatalyzed porous electrode (Prototech) is urged against the films during fuel cell assembly to form a gas diffusion backing for the thin film catalyst layer.

It should be recognized that the solubilized Nafion acts to some extent as a surfactant and dispersing agent for the supported catalyst particles. However, the dispersion of the Nafion must be controlled to provide a suitably dense film. An effective density for the present invention is obtained by simply mixing the Pt-C particles and solubilized Nafion together before the water and glycerol mixture is added.

One advantage of the dense catalyst layer herein described is improved bonding of the catalyst layer to the SPE membrane and continuity of the proton path. The dimensions of the SPE membrane increase considerably upon hydration of the hydrophilic material, whereas the relatively rigid carbon matrix of conventional gas-diffusion electrode structures does not significantly change dimensions upon hydration. Thus, where the catalyst is included within the carbon electrode struc-

ture, the continuity between the SPE surface and the catalyst interface can be adversely affected. The dense catalyst layer according to the present invention includes a hydrophilic material as a large fraction of the catalyst layer and there is less differential movement from surface expansions under hydration.

One disadvantage of forming the catalyst layer without a binder material, such as PTFE, is that suitable ionomer materials, such as Nafion, must provide structural integrity for the layer. Nafion, for example, is not melt processable and the resulting recast catalyst layer films do not have the structural integrity of commercial fluoropolymer SPE membranes. It has been found, however, that the structural integrity can be improved by heating the film to elevated temperatures for moderate amounts of time. This does cause some amount of acid-catalyzed discoloration and degradation, but the increase in structural integrity is beneficial. The film is also rendered somewhat less hydrophilic by the heating, which is beneficial at the cathode electrode where water flooding is of concern. A suitable treatment is thirty minutes exposure at 130-135°C.

Another approach to improve the structural integrity of the catalyst layer film is to introduce a binder material that readily disperses throughout the electrode structure and imparts structural integrity at low volume fractions such that performance of the electrode is not significantly impaired. Useful catalyst layers have been prepared using polyvinyl alcohol (PVA) in place of the glycerol in forming the ink. The surfactant nature of the PVA provides for adequate dispersion among the supported catalyst particles and the molecular structure acts to bind the carbon particles and Nafion agglomerates so that strong films are obtained with low weight fractions of PVA. Films have been formed with PVA concentrations of 10-12 wt% in the ink.

In another embodiment of the present invention, the integrity of catalyst layers 22, 30 is improved and acid-catalyzed degradation of the ionomer is avoided by using the Na⁺ form of the perfluorosulfonate ionomer, i.e., Nafion, to form a film for application to membrane 26 or for direct application to membrane 26, where membrane 26 is in a Na⁺ or K⁺ form. The Na⁺ perfluorosulfonate layer is cured at a temperature of at least 150°C, and preferably at least 160°C, and the catalyzed membrane assembly is thereafter converted to the H⁺, i.e., protonated, form to complete the catalyzed membrane assembly. A preferred protocol is as follows:

PROTOCOL II

1. Prepare a mixture of Nafion and catalyst as described in Step 1 of Protocol I.
2. Add a molar amount of NaOH equal to the Nafion and mix well to convert the Nafion to the Na⁺ form.
3. Form an ink as in steps 2 and 3 of Protocol I.
4. Provide a membrane of Na⁺ Nafion by soaking a protonated membrane in a solution of NaOH, fol-

lowed by rinsing and drying, or by procuring the membrane in a Na⁺ or K⁺ form.

5. Apply the ink directly to one side of the membrane. The amount of catalyst applied to the membrane is determined from the amount of ink transferred to the surface. Typically, two coats are required to obtain the desired catalyst loading. In one method of drying the ink, the ink-coated membrane is placed on a vacuum table having a fine sintered stainless steel filter on top of a heated vacuum manifold plate. A silicone blanket having a cut-out area the size of the membrane area to be inked is placed over the membrane to seal the uncovered areas of the vacuum table about the membrane. The vacuum table is operated at a temperature of at least 150°C, and preferably about 160°C, as the ink is applied. The vacuum appears to prevent distortion of the membrane from solvents in the ink and to yield a smooth, uniform film. The high-temperature application and drying appears to cure the catalyst layer to a film of high integrity and that is pliant and elastic. The second side of the membrane may be coated in the same manner.

6. Optionally, the assembly is hot pressed at 70-90 atm at 185°C for about 90 seconds.

7. The assembly is converted back to the protonated form by lightly boiling it in 0.1M H₂SO₄ and rinsing in deionized water. The assembly is air dried and combined with an uncatalyzed porous electrode as in Step 7 of Protocol I.

Alternately, the Na⁺ form of ink (Steps 1-3, above) and membrane may be used in Protocol I to form a separate catalyst film for application to the membrane.

The high-temperature casting of Na⁺ Nafion films to improve film integrity is generally suggested in Moore et al., "Procedure for Preparing Solution-Cast Perfluorosulfonate Ionomer Films and Membranes," 58 Anal. Chem., pp. 2569-2570 (1986), incorporated herein by reference. The article suggests that solvents such as dimethyl sulfoxide (DMSO) might yield equivalent properties to glycerol solvents, described above, but at lower process temperatures. The above protocol appears to yield equivalent cell performance with both DMSO and glycerol solvents. DMSO does provide a good suspension medium for the solids, however, and may form a good solution for a spray application of ink to the membrane surface.

Figures 2-7 graphically depict the performance of fuel cells prepared according to the present invention. All of the ink formulations were prepared using supported catalysts of 19.8 wt% platinum on XC-72 carbon powder (Prototech) mixed with Nafion. The cathode electrodes for mating with the catalyst layer were conventional PTFE bonded electrodes with no catalyst (Prototech). The fuel cells whose performance is shown in Figures 1-4 have cathodes prepared according to Protocol I and include conventional anodes (Prototech) with a

catalyst loading of 0.35 mg Pt/cm² plus a sputter coat of 500 Å Pt. It will be understood that conventional anode electrodes were used to provide performance comparisons of cathode electrodes.

The anode catalyst loading is not expected to have any significant effect on cell performance. Indeed, the fuel cells whose performance is shown in Figures 5 and 6 include high temperature catalytic layers on both the cathode and anode faces of the membrane. both catalytic layers incorporated equivalent catalyst loadings, e. g., 0.13 mg Pt/cm², for a total cell loading of, 0.26 mg Pt/cm² of electrode surface.

Figure 2 graphically depicts the voltage vs. current density curves for fuel cells having conventional Prototech anodes, Nafion 117 (7 mil thick) SPE membrane, and a cathode assembly with a catalyst layer produced by mixing Pt/C catalyst and Nafion and hot pressed onto the SPE membrane. Catalyst loadings of 0.20 and 0.35 mg Pt/cm² are compared using both neat oxygen and air as the oxidant. It is readily seen that the thinner catalyst layer (0.20 mg Pt/cm²) performs somewhat better than the thicker film (0.35 mg Pt/cm²) at higher current densities. At the higher current densities, the active region of the catalyst layer narrows and less of the film thickness is utilized, wherein mass transfer losses increase in the thicker film and performance decreases. The low partial pressure of oxygen in air as compared to neat oxygen induces an earlier and steeper fall off in performance at the higher current densities.

Figure 3 graphically depicts the voltage vs. current density curves for fuel cells constructed as the fuel cells of Figure 2, except that the SPE membrane is Membrane "C" (a perfluorosulfonate membrane from Chlorine Engineers Inc. of Japan). Catalyst loadings of 0.15 and 0.22 mg Pt/cm² are compared, again using both neat oxygen and air as oxidizers. The results are consistent with the results shown with Nafion 117 forming the SPE membrane, with lower potentials from the thicker film at higher current densities.

The performance of the fuel cells depicted in both Figures 2 and 3 approach those of fuel cells fabricated with conventional Prototech cathode assemblies or of assemblies using unsupported Pt catalyst with much higher Pt loadings. Figure 4 particularly compares the cell voltage vs. current density performance of a thin catalyst with a loading of 0.15 mg Pt/cm² with a cell having the catalyst included in a carbon electrode to a loading of 0.35 mg Pt/cm² with an extra sputter coating of 500 Å Pt. The substantial similarity in performance is readily apparent.

The performance of fuel cells formed by a direct application of a Na⁺ ink to a Na⁺ membrane is shown in Figures 5 and 6. Figure 5 depicts the performance of the high-temperature, thin film formed on Membrane "C" according to Protocol II, wherein the cell performance on oxygen is at least equal to the performance of the separate thin film cell shown in Figure 4. Figure 6 depicts the performance of the high-temperature, thin film

formed on a "Dow" membrane according to Protocol II, wherein an improved cell performance is obtained. The "Dow" membrane is a proton conducting membrane available from the Dow Chemical Company. It is quite significant that a low Pt loading of 0.13 mg Pt/cm² is effective to generate current densities of above 3 A/cm² at a cell voltage higher than 0.4V for operation on pressurized oxygen and, particularly, that such a low loading is effective to reach a cell voltage of 0.65V at 1 A/cm² for cells operated on pressurized air.

To further illustrate the significant increase in catalyst utilization efficiency afforded by the present invention, Figure 7 depicts cell voltage as a function of the specific activities of the cathodes (A/mgPt) for fuel cells with four different cathode catalyst configurations: (1) a thin film catalyst loading of 0.15 mg Pt/cm², as taught herein; (2) a high-temperature thin film with a catalyst loading of 0.13 mg Pt/cm² applied directly to the membrane as an ink; (3) a commercial Prototech electrode with a catalyst loading of 0.35 mg Pt/cm² and 500 Å Pt coating; and (4) GE/HS-UTC-type cell with 4 mg Pt/cm² (unsupported) hot pressed into the SPE. It should be noted that the GE/HS-UTC-type cell has hardware, membrane design, and operating conditions that are significantly different from the other cells and its performance comparison is merely illustrative. The differences in the specific activities for each type of electrode are clearly significant, with the thin film supported catalyst layers according to the present invention being the most efficient utilization of the Pt catalyst.

Thus, it will be appreciated that the present invention obtains a high catalyst utilization by the improved construction of the catalyst layer with low Pt loadings primarily involving increased contact area between the polymer electrolyte and the Pt catalyst clusters. The contact area is increased in two ways. First, the supported catalyst and the ionomeric additive are cast together to form the catalytic layer. Second, the hydrophobic additive is completely eliminated and the ionomer is uniformly dispersed throughout the catalyst layer. The latter is accomplished by blending the solubilized ionomer and the platinized carbon into a homogeneous "ink," from which the thin film catalyst layer is formed.

Figures 2 and 3 illustrate the significance of film thickness affecting proton penetration and gas access and the resulting cell performance. As current density increases, the active catalyst region narrows. Thus, the oxidizer gas must diffuse through the inactive portion of the catalyst layer and, in the case of air, the mass transfer limitation significantly increases the overpotential. An electrode thickness roughly equivalent to that of the active region at a particular current density would provide an optimum performance at that current density. For example, with 20 wt% Pt/C supported catalyst and a catalyst layer fabricated in accordance with the above principles, reasonable fuel cell performance is obtained down to about 0.1 mg Pt/cm², after which it falls off in proportion to further decrease in catalyst loading. Con-

comitant film thicknesses are in the range of 1-10 μ, and preferably 2 to 3 μ. It is expected that catalyst loadings as low as 0.05 mg Pt/cm² may be used for an anode catalyst layer without significant loss of performance. Improved performance might be obtained from a given catalyst layer thickness if a higher Pt loading could be included without increasing the thickness of the supported catalyst.

The foregoing description of the preferred embodiments of the invention have been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

Claims

1. A solid polymer electrolyte membrane assembly for separating anodic and cathodic electrode backings in a gas reaction fuel cell, wherein the improvement consists essentially of a solid polymer electrolyte membrane and a composite film of a supported platinum catalyst and a proton conducting ionomer with a thickness less than about 10 μm, said catalyst being uniformly dispersed therein with a platinum loading less than about 0.35 mgPt/cm², where said film is bonded to said solid polymer electrolyte membrane.
2. A membrane assembly according to claim 1, where said platinum loading is greater than 0.1 mg/cm².
3. A membrane assembly according to claim 1, wherein said proton conducting material is the same material forming said solid polymer electrolyte.
4. A membrane assembly according to claim 1, wherein said composite film containing proton conducting ionomer is formed from a perfluorosulfonate ionomer by drying a solution containing a Na⁺ form of said ionomer at a temperature of at least 150°C and thereafter converting said Na⁺ form to a protonated form.
5. A membrane assembly according to claim 4, wherein said solid polymer electrolyte membrane is formed by converting a membrane of a Na⁺ or K⁺ form of perfluorosulfonate ionomer to a protonated form with said composite film in said Na⁺ form.

6. A method for fabricating a solid polymer electrolyte membrane assembly for separating anodic and cathodic backings in a gas reaction fuel cell, comprising the steps of:

uniformly dispersing a supported Pt catalyst in a perfluorosulfonate ionomer;
forming a thin film of said ionomer with said catalyst; and
transferring said film to a surface of a solid polymer electrolyte membrane.

7. A method according to claim 6, further including the step of furnishing said perfluorosulfonate ionomer in a Na⁺ form.

8. A method according to claim 7, further including the step of furnishing said membrane as a perfluorosulfonate material in a Na⁺ or K⁺ form.

9. A method according to claim 7, further including the step of converting said thin film of said ionomer to a protonated form of said ionomer.

10. A method according to claim 6, wherein the step of transferring said film comprises the steps of:

forming said film over a release blank to a selected catalyst loading;
hot pressing said film into said surface of said solid polymer electrolyte membrane to cure said film and adhere said film to said surface; and
removing said release blank from said film.

11. A method according to claim 10, wherein the step of dispersing said catalyst in said ionomer further includes the steps of:

adding a solvent to said ionomer and said catalyst to obtain a mixture with a viscosity effective for forming said film;
agitating said mixture to disperse said catalyst.

12. A method for fabricating a solid polymer electrolyte membrane assembly for separating anodic and cathodic electrode backings in a gas reaction fuel cell, comprising the steps of:

furnishing a perfluorosulfonate ionomer in a Na⁺ form;
uniformly dispersing a supported Pt catalyst and a solvent in said Na⁺ form of said ionomer to form an ink;
forming a film of said ink containing a predetermined amount of said catalyst on a surface of a solid polymer electrolyte membrane;
heating said film of said ink to a temperature of

at least 150°C for a time effective to dry said ink; and converting said Na⁺ form of said perfluorosulfonate ionomer to a protonated form.

13. A method according to claim 12, wherein the step of furnishing said perfluorosulfonate ionomer in a Na⁺ form includes the step of adding NaOH to a protonated form of said perfluorosulfonate ionomer.

14. A method according to claim 13, further including the step of furnishing said solid polymer electrolyte membrane in a Na⁺ form.

15. A method according to claim 12, further including the step of maintaining said membrane planar on a vacuum table while forming said film of said ink on said membrane.

20 Patentansprüche

1. Feste polymerelektrolytische Membranzusammenstellung zum Trennen anodischer und kathodischer Elektrodenstrukturen in einer Gasreaktionsbrennstoffzelle, wobei die Verbesserung im wesentlichen aus einer festen Polymerelektrolytmembran und aus einem zusammengesetzten Film eines unterstützten Platinkatalysators und aus einem protonenleitenden Ionomer mit einer Dicke von weniger als 10 µm besteht, wobei der Katalysator darin gleichmäßig mit einer Platinimprägnierung von weniger als 0,35 mg Pt/cm² verteilt und dieser Film an die feste Polymerelektrolytmembran gebunden ist.
2. Membranzusammenstellung gemäß Anspruch 1, bei der die Platinimprägnierung mehr als 0,1 mg/cm² beträgt.
3. Membranzusammenstellung nach Anspruch 1, bei der das protonenleitende Material dasselbe Material ist, welches den festen Polymerelektrolyten bildet.
4. Membranzusammenstellung gemäß Anspruch 1, bei der der zusammengesetzte, einen protonenleitenden Ionomer enthaltende Film aus einem Perfluorosulfonationsomer durch Trocknen einer Lösung enthaltend eine Na⁺-Darstellung des Ionomers bei einer Temperatur von wenigstens 150°C und einem anschließenden Konvertieren der Na⁺-Darstellung in eine protonierte Darstellung gebildet ist.
5. Membranzusammenstellung gemäß Anspruch 4, bei der die feste Polymerelektrolytmembran durch Konvertieren einer Membran einer Na⁺- oder K⁺-Darstellung eines Perfluorosulfonationsomers in eine protonierte Darstellung mit dem zusammengesetzten Film in der Na⁺-Darstellung gebildet ist.

6. Verfahren zur Herstellung einer festen Polymer-elektrolytmembranzusammenstellung zum Trennen anodischer und kathodischer Strukturen in einer Gasreaktionsbrennstoffzelle mit folgenden Schritten:
- 5 Gleichmäßiges Verteilen eines unterstützten Pt-Katalysators in einem Perfluorosulfonationsmonomer;
Bilden eines dünnen Filmes des Polymers mit dem Katalysator; und 10
Übertragen des Filmes auf eine Oberfläche einer festen Polymerelektrolytmembran.
7. Verfahren gemäß Anspruch 6, welches ferner den Schritt des Bereitstellens des Perfluorosulfonationsmonomers in einer Na⁺-Darstellung beinhaltet. 15
8. Verfahren nach Anspruch 7, welches ferner den Schritt des Bereitstellens der Membran als ein Perfluorosulfonatmaterial in einer Na⁺-oder K⁺-Darstellung umfaßt. 20
9. Verfahren nach Anspruch 7, welches ferner den Schritt des Konvertierens des Dünnsfilmes des Ionomers in eine protonierte Darstellung des Ionomers umfaßt. 25
10. Verfahren nach Anspruch 6, bei dem der Schritt des Übertragens des Filmes folgende Schritte aufweist: 30
Bilden des Filmes auf einem Transferstück für eine vorbestimmte Katalysatorimprägnierung;
Heißpressen des Filmes in die Oberfläche der festen Polymerelektrolytmembran, um den Film auszuhärten und diesen Film mit der Oberfläche zu verbinden; und
Entfernen des Transferstückes von dem Film.
11. Verfahren nach Anspruch 10, bei welchem der Schritt des Verteilens des Katalysators in dem Ionomer ferner folgende Schritte umfaßt: 40
Hinzufügen eines Lösungsmittels zu dem Ionomer und dem Katalysator, um eine Mischung mit einer für die Filmbildung entsprechenden Viskosität zu erhalten;
Verrühren der Mischung, um den Katalysator zu verteilen. 45
12. Verfahren zur Herstellung einer festen Polymerelektrolytmembranzusammenstellung zum Trennen anodischer und kathodischer Elektrodenstrukturen einer Gasreaktionsbrennstoffzelle mit den Schritten: 55
Bereitstellung eines Perfluorosulfonationsmonomers in einer Na⁺-Darstellung;
- Gleichmäßiges Verteilen eines unterstützten Pt-Katalysators und eines Lösungsmittels in der Na⁺-Darstellung des Ionomers, um eine Tinte zu bilden;
Bilden eines Films aus der Tinte mit einem vorbestimmten Gehalt des Katalysators auf einer Oberfläche einer festen Polymerelektrolytmembran;
Aufheizen des Filmes der Tinte auf eine Temperatur von mindestens 150°C für eine zum Trocknen der Tinte ausreichende Zeit; und
Konvertieren der Na⁺-Darstellung des Perfluorosulfonationsmonomers in eine protonierte Darstellung.
13. Verfahren nach Anspruch 12, bei dem der Schritt des Bereitstellens des Perfluorosulfonationsmonomers in einer Na⁺-Darstellung den Schritt des Hinzufügens von NaOH in eine protonierte Darstellung des Perfluorosulfonationsmonomers beinhaltet.
14. Verfahren nach Anspruch 13, welches ferner den Schritt des Bereitstellens der festen Polymerelektrolytmembran in einer Na⁺-Darstellung beinhaltet.
15. Verfahren nach Anspruch 12, welches ferner den Schritt des Belassens der Membran planar auf einem Vakuumtisch beinhaltet, während der Film der Tinte auf der Membran gebildet wird.

Revendications

1. Un système de membrane électrolytique de polymère solide pour séparer les supports d'électrode anodique et cathodique dans une pile à combustible à réaction de gaz, dans lequel l'amélioration consiste principalement en une membrane électrolytique de polymère solide et en un film composite de catalyseur de platine supporté et d'un ionomère conducteur de proton d'une épaisseur inférieure à environ 10 µm, ledit catalyseur étant dispersé uniformément en son sein avec une charge de platine inférieure à environ 0,35 mg de Pt/cm², et dans lequel ledit film est lié à ladite membrane électrolytique de polymère solide.
2. Un système de membrane selon la revendication 1, dans lequel ladite charge de platine est supérieure à 0,1 mg/cm².
3. Un système de membrane selon la revendication 1, dans lequel ladite substance conductrice de proton est la même substance que celle qui forme l'électrolyte de polymère solide.
4. Un système de membrane selon la revendication 1, dans lequel ledit film composite contenant l'ionomère

- re conducteur de proton est formé à partir d'un ionomère perfluorosulfonate par séchage d'une solution contenant une forme Na^+ dudit ionomère à une température d'au moins 150°C suivi de la transformation de ladite forme Na^+ en la forme protonée.
- 5
5. Un système de membrane selon la revendication 4, dans lequel ladite membrane électrolytique de polymère solide est formée en transformant une membrane sous la forme Na^+ ou K^+ d'un ionomère perfluorosulfonate en forme protonée avec ledit film composite sous ladite forme Na^+ .
- 10
6. Une méthode de fabrication d'un système de membrane électrolytique de polymère solide pour la séparation des supports cathodique et anodique dans une pile à combustible à réaction de gaz, comprenant les étapes de:
- 15
- dispersion uniforme de catalyseur de platine supporté dans un perfluorosulfonate ionomère;
 - formation d'un film mince dudit ionomère avec ledit catalyseur; et
 - transfert dudit film sur la surface d'une membrane électrolytique de polymère solide.
- 20
- 25
7. Une méthode selon la revendication 6, comprenant en outre l'étape d'apport dudit perfluorosulfonate ionomère sous forme Na^+ .
- 30
8. Une méthode selon la revendication 7, comprenant en outre l'étape d'apport ladite membrane sous forme d'une substance perfluorosulfonate sous forme Na^+ ou K^+ .
- 35
9. Une méthode selon la revendication 7, comprenant en outre l'étape de transformation dudit film mince dudit ionomère en la forme protonée dudit ionomère.
- 40
10. Une méthode selon la revendication 6, dans laquelle l'étape de transformation dudit film comprend les étapes de:
- 45
- formation dudit film sur une feuille antiadhérente à une charge de catalyseur choisie;
 - compression à chaud dudit film sur ladite surface de ladite membrane électrolytique de polymère solide pour durcir ledit film et faire adhérer ledit film sur ladite surface; et
 - détachement de ladite feuille antiadhérente dudit film.
- 50
- 55
11. Une méthode selon la revendication 10, dans laquelle l'étape de dispersion dudit catalyseur dans ledit ionomère comprend en outre les étapes de:
- addition d'un solvant audit ionomère et audit
- catalyseur pour obtenir un mélange d'une viscosité convenable pour la formation dudit film;
- agitation dudit mélange pour disperser ledit catalyseur.
12. Une méthode de fabrication d'un système de membrane électrolytique de polymère solide pour séparer les supports anodiques et cathodique d'électrode dans une pile à combustible à réaction gazeuse comprenant les étapes de:
- apport d'un perfluorosulfonate ionomère sous forme de Na^+ ;
 - dispersion uniforme d'un catalyseur de platine supporté et d'un solvant dans ladite forme Na^+ dudit ionomère pour obtenir une encre;
 - formation d'un film de ladite encre contenant une quantité prédéterminée dudit catalyseur sur une des faces d'une membrane électrolytique de polymère solide;
 - chauffage dudit film de ladite encre à une température d'au moins 150°C pendant une durée suffisante pour sécher ladite encre et transformation de ladite forme Na^+ dudit perfluorosulfonate ionomère en forme protonée.
13. Une méthode selon la revendication 12, dans laquelle l'étape d'apport dudit perfluorosulfonate ionomère sous forme Na^+ comprend l'étape d'addition de NaOH à la forme protonée dudit perfluorosulfonate ionomère.
14. Une méthode selon la revendication 13, comprenant en outre l'étape d'apport de ladite membrane d'électrolytique polymère solide sous forme Na^+ .
15. Une méthode selon la revendication 12, comprenant en outre l'étape de maintien de ladite membrane à plat sur une table d'aspiration pendant qu'on forme ledit film de ladite encre sur ladite membrane.

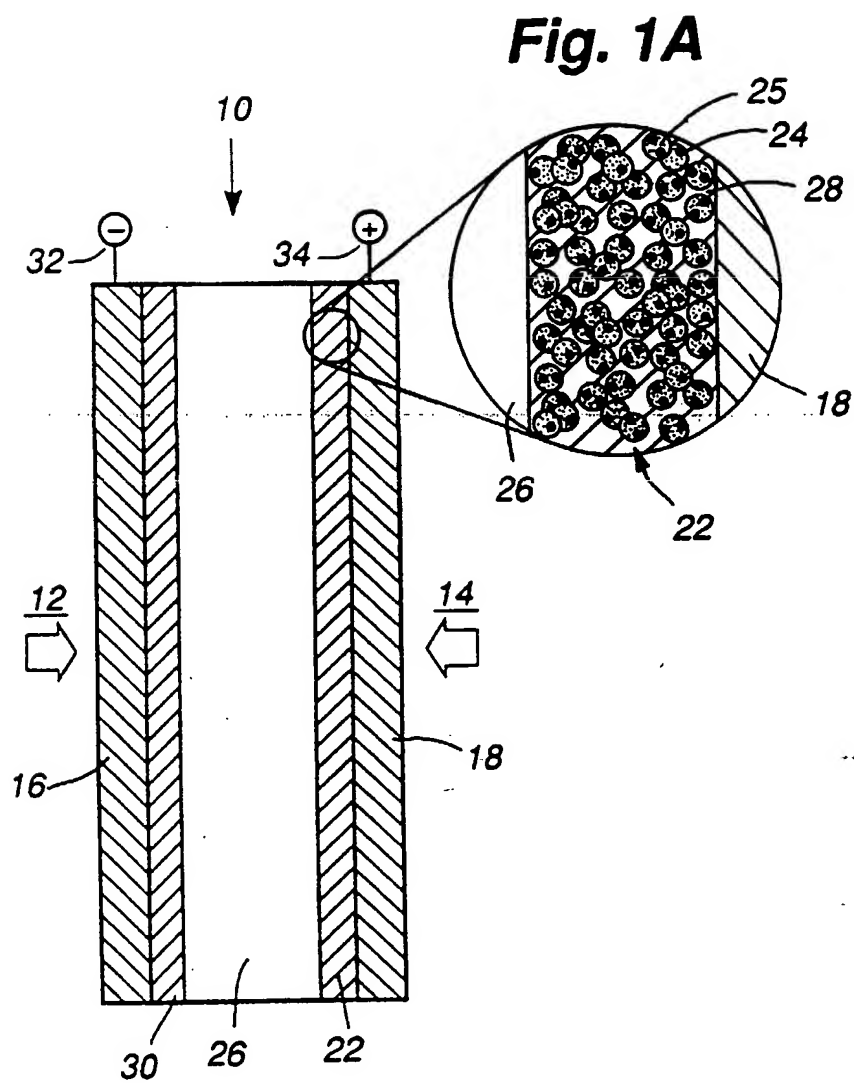
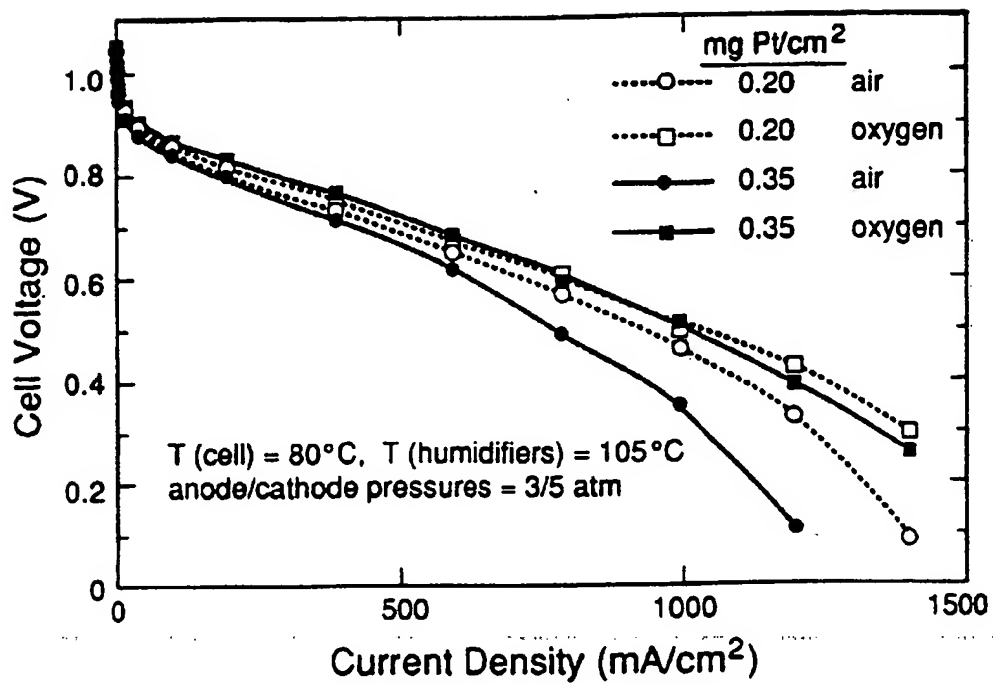
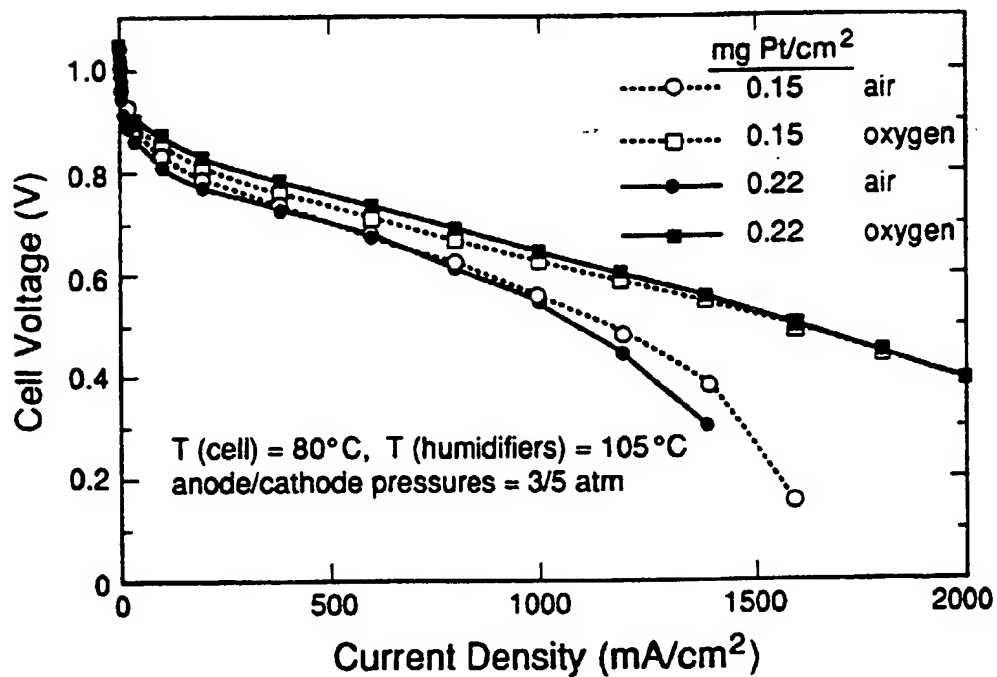
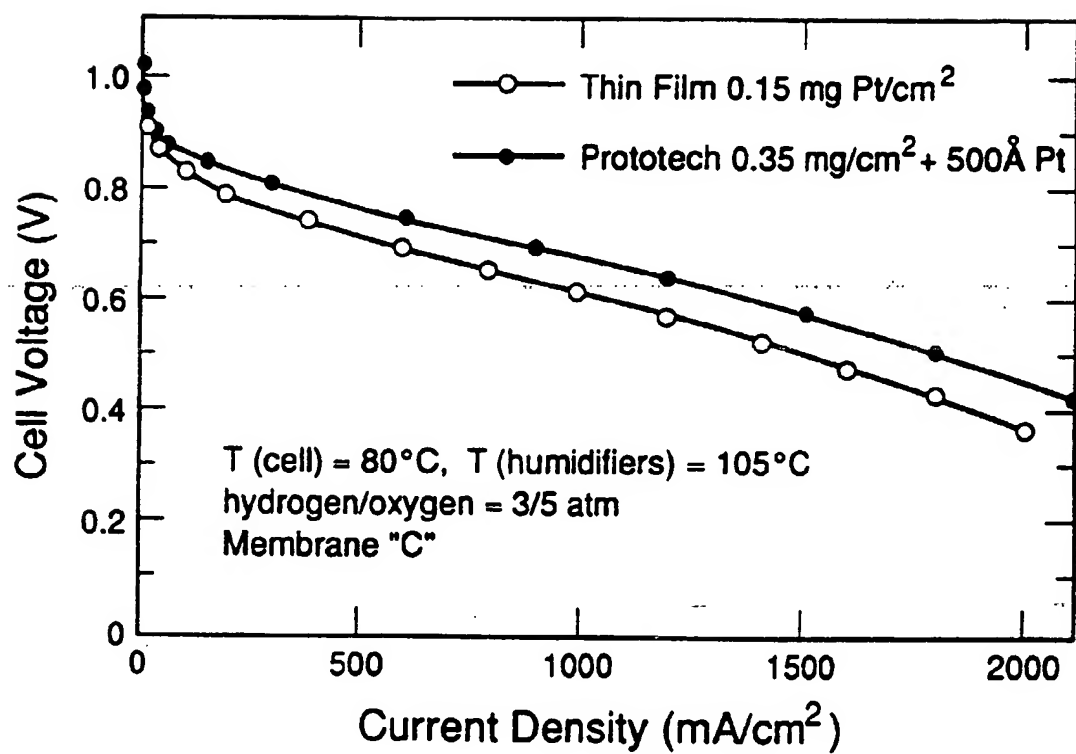
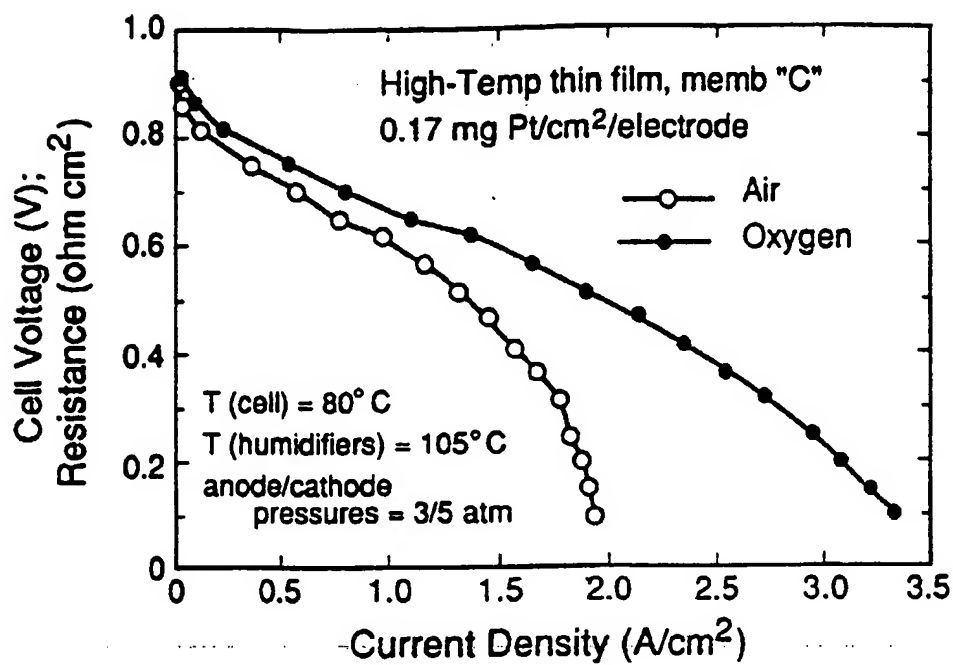
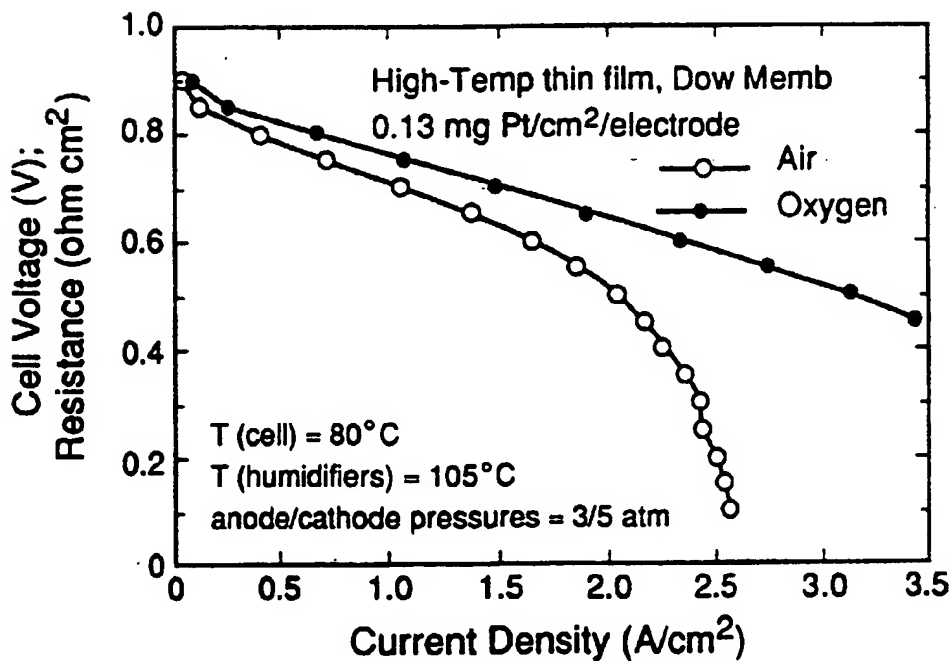
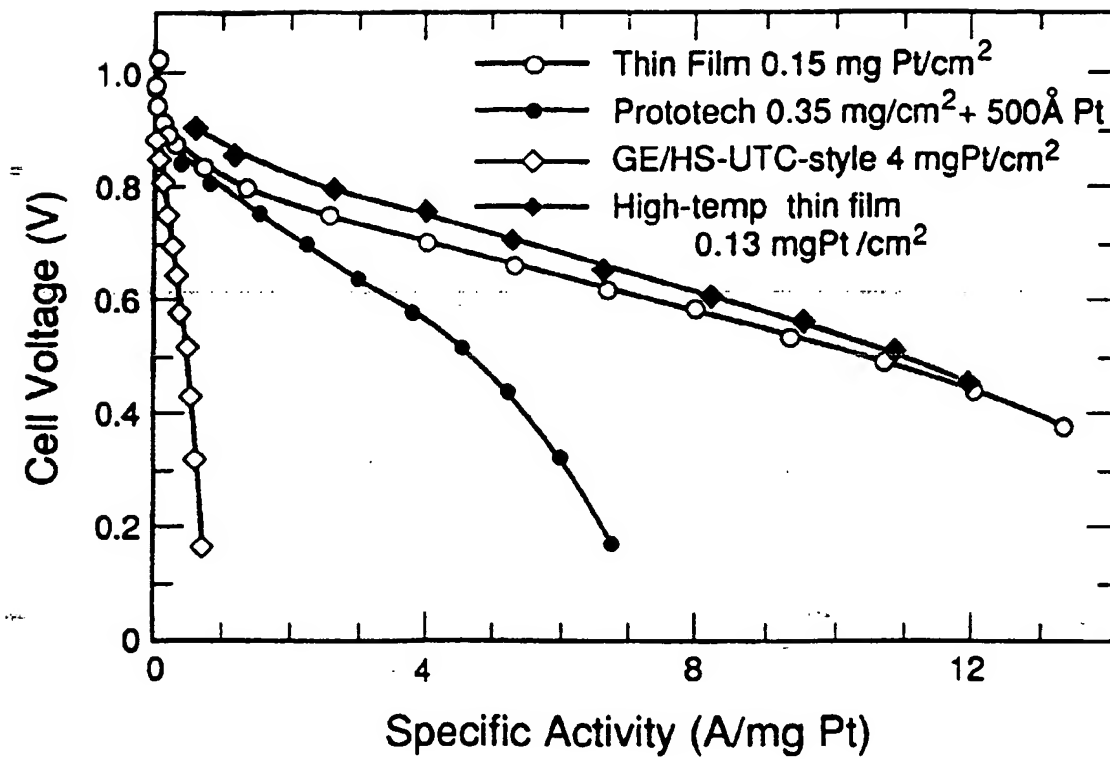


Fig. 1

**Fig. 2****Fig. 3**

**Fig. 4**

**Fig. 5****Fig. 6**

**Fig. 7**